



Short communication

Performance of an Electrochemical double layer capacitor based on coconut shell active material and ionic liquid as an electrolyte

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H I G H L I G H T S

- ▶ Coconut raw materials were tested as electrodes for EDLC.
- ▶ Ionic Liquid and Et₄NBF₄/AN were used as electrolyte and compared.
- ▶ The highest capacitances for Carbon/Ionic liquid system have been observed.
- ▶ Optimisation of the mass electrodes improve characteristics of the EDLC.

A R T I C L E I N F O

Article history:

Received 26 April 2012

Received in revised form

28 September 2012

Accepted 16 November 2012

Available online 28 November 2012

Keywords:

Room temperature ionic liquid

EMImBF₄

Electrochemical double layer capacitor

(EDLC)

Activated carbon

A B S T R A C T

EDLCs based on the modified coconut shell raw material were manufactured with 1-Ethyl-3-methylimidazolium tetrafluoroborate (EMImBF₄) as an electrolyte and a typical organic electrolyte based on acetonitrile. Three types of modification of the carbon material with different micro- to mesopore ratios were applied as the positive or negative electrode and tested. Obtained results showed different characteristic capacitances of 150–350 F g⁻¹, strongly dependent on the type of carbon material. Asymmetric EDLCs were manufactured from different carbon materials as positive and negative electrodes and a mass electrode fitting provided with an EDLC working at 3 V with a specific energy of 68.6 Wh kg⁻¹ and power density of 36 W kg⁻¹.

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1. Introduction

Electrochemical Double Layer Capacitors (EDLCs), also called supercapacitors, have attracted much attention for decades [1–3]. EDLCs are energy storage devices that collect energy at the electrode/electrolyte double layer interphase. High surface carbon-based materials have been used as electrode material [4–6] and several types of electrolytes are regarded to be suitable: aqueous, nonaqueous and solvent-free [7–9]. Potential application of EDLCs is attractive for power back-up systems, as well as highly-efficient and high-power supporting devices for hybrid engine vehicles [10–12]. To produce highly-efficient devices several factors should be taken into account, such as surface area and structure of carbon materials, as well as pore distribution and electrolyte properties.

Such proper combinations are crucial factors of electrochemical capacitor performance [5]. In addition, optimum conditions should be provided for the positive and negative electrode separately, which influences capacitance and voltage characteristics of EDLCs [13]. An important aspect of the carbon active material investigated in this study is the chemical structure of the electrode materials, as nitrogen and oxygen contents can significantly influence capacitive properties of the electrode/electrolyte combination [14,15]. Enrichment of carbon materials may be provided by an addition of a nitrogen-rich chemical compound, such as melamine, and thermal pyrolysis of selected precursors.

Ionic liquids are a class of chemical compounds investigated for several decades. Their special properties result from their structure, they are liquids over a wide range of temperatures and they consist entirely of ions. ILs have been studied in various fields of chemistry: they may serve as solvents for chemical reactions [16,17] as well as electrolytes in electrochemical devices [18–21]. Some of the

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examples of ionic liquids are considered as suitable for EDLC applications [22–25]. Imidazolium, pyrrolidinium, sulfonium or piperidinium based cations and anions such as tetrafluoroborate (BF_4^-) or bis(trifluoromethanesulfonyl)imide (TFSI) offer the highest electrochemical stability windows, which facilitates the relatively higher operation voltage of EDLC and as a consequence more energy can be stored in a single electrochemical cell.

This paper concerns a potential application of 1-Ethyl-3-methylimidazolium tetrafluoroborate (EMImBF₄) as an electrolyte in EDLCs. The EDLCs tested are based on carbon materials obtained from coconut raw material. These materials were modified and studied before with aqueous based electrolytes yielding as much as 300–350 Fg^{-1} specific capacitance [26]. Three types of carbon materials with different rates of micro- to mesopores were used as electrodes to obtain EDLCs of best performance parameters.

2. Experimental

2.1. Materials

High purity 1-Ethyl-3-methylimidazolium tetrafluoroborate (EMImBF₄) was purchased from Aldrich and dried before use under vacuum at 60 °C. Chromatographic grade acetonitrile (Aldrich) was used as received. Tetraethylammonium tetrafluoroborate (Et_4NBF_4) (Aldrich) was purified by ethanol crystallization and dried under vacuum at 60 °C.

Carbon materials were prepared by pyrolysis of the coconut shell precursor at 500 °C and activated in KOH mixture at 900 °C with a C/KOH ratio of 1:4. Melamine as a nitrogen heteroatom source was added during the process ($T_{\text{decom}} = 347$ °C). Several materials were obtained with different micropore to mesopore volume rates $V_{\text{mic}}/V_{\text{mes}}$ ranging from 0.082 to 0.295 (AC082, AC170 and AC295) and selected for the present study. The carbon materials were prepared from the same raw material using the same procedures of pyrolysis and activation. Carbon AC170 was obtained using additions of melamine solution before the pyrolysis process. AC082 was obtained by double pyrolysis: first the raw material was pyrolyzed and then after melamine addition the process was repeated. AC295 as a reference material was prepared without melamine addition. Details of the carbon material preparation were published in a previous paper [26]. The specific surface of obtained activated carbons was over 3000 $\text{m}^2 \text{g}^{-1}$ (BET). The chemical structure of the materials tested was characterized by X-ray photoelectron spectroscopy (XPS). Capacitor electrodes were prepared from a composition of acetylene black (AB) and polytetrafluoroethylene (PTFE) water suspension as a binder material. The composition of AC:AB:PTFE electrodes was 88:10:2 %wt. All the constituents were mixed and pressed. Pellets of ca. 10 mg and 12 mm in diameter were dried at 105 °C and soaked with electrolytes. Two types of electrolytes were tested: (i) EMImBF₄, and (ii) 1M Et_4NBF_4 solution in acetonitrile (AN) as a common nonaqueous electrolyte.

2.2. Measurements

Electrochemical capacitors were manufactured in a three-electrode Swagelok-type compartment filled with electrolyte in a glove-box chamber. The reference electrode was silver wire covered electrochemically by silver chloride (Ag/AgCl). The reference electrode was placed in the space between the positive and negative electrode to facilitate control of potential changes in the positive and negative cell space separately. Potentiodynamic measurements (at sweep rates of 2–100 mV s^{-1}) and galvanostatic measurements (0.2–1 Ag^{-1}) were taken using a BT200 device (Arbin Instruments) in a three-electrode system. In all measurements potentials of positive and negative electrodes were

Table 1

Structural parameters of carbon materials tested [26].

Sample	Surface area BET [$\text{m}^2 \text{g}^{-1}$]	V_{total} [$\text{cm}^3 \text{g}^{-1}$]	V_{mic}	V_{mes}	$V_{\text{mic}/\text{mes}}$	C	O	N
						Atomic %		
AC295	3261	2.032	0.464	1.568	0.295	79.6	20.1	0.3
AC170	3162	2.219	0.324	1.895	0.170	78.9	19.2	2.2
AC082	3338	2.499	0.190	2.308	0.082	83.9	13.2	2.9

controlled separately. Maximum operation voltage of the cell in the two electrode regime was max. 3 V. In case of cyclic voltammetry measurements, capacitances were calculated from the equation $C = I(\text{d}V/\text{d}t)^{-1} m_{\text{carb}}^{-1}$ where I —current, $\text{d}V/\text{d}t$ = sweep rate of the potential of an individual electrode, m_{carb} —mass of active carbon in the individual electrode. In all cases of three electrode measurements the potential change of the full cell (3 V) was equivalent to a symmetric change of 1.5 V for an individual electrode. In case of galvanostatic measurements, capacitance was obtained from the same equation $C = I(\Delta V/\Delta t)^{-1} m_{\text{carb}}^{-1}$, I = constant current $\Delta V/\Delta t$ —was the slope of potential change of the individual electrode. Electrochemical impedance spectroscopy (EIS) was performed with an Autolab 30 FRA2 (Eco-Chemie, the Netherlands) applying a 10 mV amplitude signal and frequency range of 100 kHz–1 mHz. The three-electrode cell was also used to separately investigate cathodic and anodic properties of the carbon/electrolyte interphase. Gravimetric capacitance was calculated assuming the simplest equivalent circuit, consisting of resistance and capacitance connected in a series. Capacitance was obtained according to the equation $C = (2\pi f Z_{\text{im}})^{-1} m_{\text{carb}}^{-1}$, where: Z_{im} —imaginary impedance, f —frequency and m_{carb} —mass of active carbon. All measurements were taken at ambient temperature.

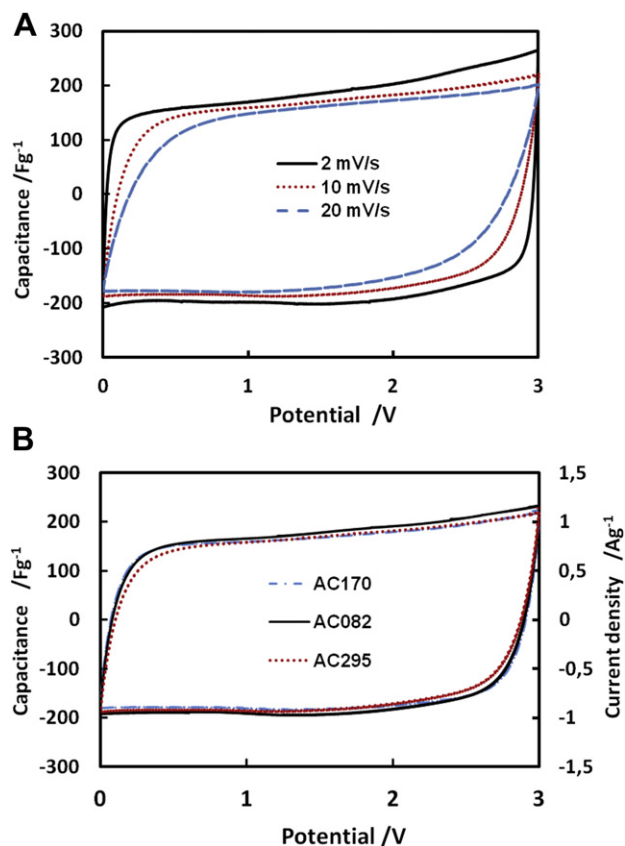


Fig. 1. Cyclic voltammetry of EDLC based on carbon AC295 at different sweep rates (A) and symmetric EDLCs based on three different carbons - AC295, AC170 and AC082 at equal sweep rate of 10 mV s^{-1} (B). EMImBF₄ as electrolyte. Masses of active carbon 9.0–8.9 mg.

3. Results and discussion

3.1. Symmetric EDLC

Table 1 presents structural parameters of selected carbon materials. Characteristic properties include different micro- and mesopore distribution, contents of nitrogen and oxygen atoms. Micro- to mesopore volume distribution ($V_{\text{mic}}/V_{\text{mes}}$) in the selected materials ranges from 0.082 (AC082 sample) to 0.295 (AC295 sample). The number of nitrogen heteroatoms increases in investigated materials in the following order AC082 > AC170 > AC295, whereas an opposite trend is observed for oxygen atom contents.

Fig. 1 presents cyclic voltammograms obtained in the two-electrode system for symmetric EDLCs with EMImBF₄ as an electrolyte. Fig. 1A shows the application of carbon materials based on AC295, at different sweep rates ranging from 2 to 20 mV s⁻¹. Similar results were obtained for the other carbons tested. A box-like shape could be observed in all cases, suggesting a typical capacitor behaviour. Fig. 1B presents all of the carbons tested as material electrodes at the same sweep rate of 10 mV s⁻¹. For all cases similar

capacitances of 150 Fg⁻¹ were recorded at ca. 1 Ag⁻¹ current density. However, inspection of Fig. 2, presenting the same experiments (at 5 mV s⁻¹ for separately controlled negative and positive electrodes) evidently shows different behaviour of carbon materials used as positive and negative electrodes. Results describing the negative electrode presented on Fig. 2 indicated a slightly better characteristic for carbon AC170 with $V_{\text{mic}}/V_{\text{mes}}$ of 0.170 applied as the negative electrode interacting with 1-ethylmethyl-3-imidazolium cation (EMIm⁺). The effect of the BF₄⁻ anion on the positive electrode characteristics is more varied. Fig. 2A and C shows that electrodes applied therein exhibit better capacitances than carbon AC170. A similar behaviour may be observed in Fig. 3A and B. Fig. 3A shows the effect of sweep rate on the gravimetric capacitance of cells in symmetric EDLCs based on AC295, AC170 and AC082. In all cases the curves show a similar tendency and capacitances decreased significantly after reaching 50 mV s⁻¹. Fig. 3B presents results for the negative and positive application of carbon materials separately. It is clearly visible that positive electrodes exhibit better characteristics in all the carbons, which can be explained in terms of an interaction of the BF₄⁻ cation with the carbons tested. Gravimetric capacitances were of 200–260 Fg⁻¹ of active material, whereas negative electrode capacitances were below 200 Fg⁻¹.

The capacitance changes of positive and negative electrodes based on the AC170 sample can be observed on Fig. 3B. The flat and parallel course of both curves indicates balanced dynamic charge

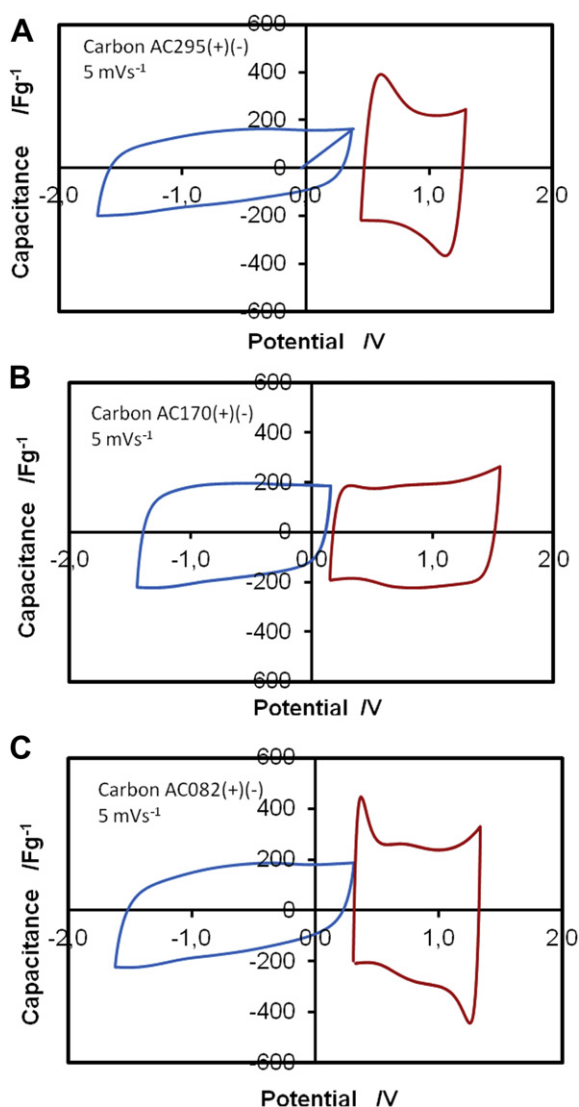


Fig. 2. Cyclic voltammetry of EDLC based on different types of carbon materials (A) AC295, (B) AC170 and (C) AC082. Comparison of positive and negative electrode behaviours. EMImBF₄ as electrolyte. Masses of active carbon 9.0–8.9 mg.

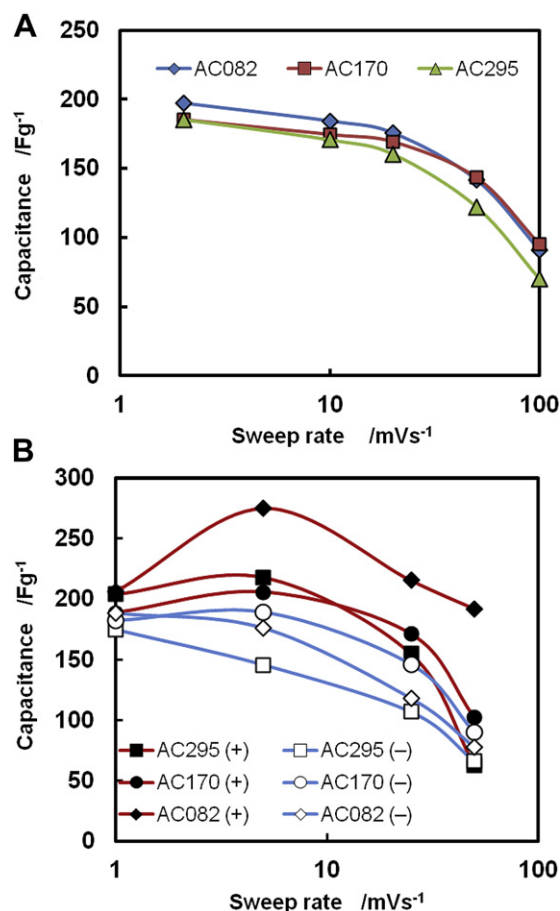


Fig. 3. Capacitance of carbon materials in symmetric EDLCs with different types of carbons measured by cyclic voltammetry vs scan rate. Full cell (A) and separately for positive (+) and negative (-) electrodes (B). Electrolyte: EMImBF₄. Masses of active carbon 9.0–8.9 mg.

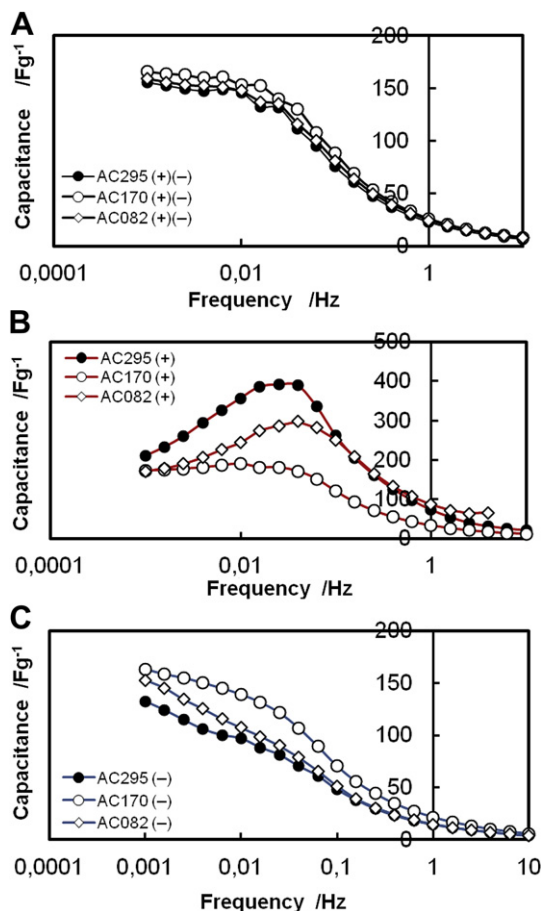


Fig. 4. Impedance analysis of symmetric EDLCs based on different types of carbons: symmetric full cell (A), positive electrode (B) and negative electrode (C). Electrolyte: EMImBF₄. Masses of active carbon 9.0–8.9 mg.

propagation, resulting in less influence of sweep rate on capacitance, being most evident on Fig. 3A for the AC170 sample.

The results mentioned above can also be concluded from the Electrochemical Impedance Spectroscopy (EIS) analysis. Fig. 4 presents the frequency dependence of capacitance derived from the symmetrically built capacitor (Fig. 4A) and shows different characteristics of the tested materials as the positive (Fig. 4B) and negative electrodes (Fig. 4C). In all cases capacitances of the symmetric capacitor show very similar values of 150–170 Fg⁻¹. Inspection of Fig. 4B and C shows different behaviour of the materials applied as the negative or positive electrodes. Results

presented here confirm the previous conclusions. Carbon AC295 shows gravimetric capacitances as high as 350–400 Fg⁻¹. The higher specific capacitances could be explained in terms of the chemical nature of carbon applied; however, neither oxygen nor nitrogen content can be regarded as responsible factors for such a behaviour. Table 2 summarises values of gravimetric capacitances for three types of carbons tested in two electrolytes. Inspection of the table points at better capacitances of all tested carbons in the ionic liquid than in a solution of Et₄NBF₄ in acetonitrile (AN) in both positive and negative electrodes. Such a behaviour is rather surprising, but has been reported in the literature [27,28]. A possible explanation may be discussed in term of the solvation process as well as pore size fitting. All of the carbon materials in fact have a rather narrow range of pore diameter [26]. The range of pore size is 2–7 nm in case of AC082 and AC170, and 2–5 nm in case of AC295. A significant difference of capacitance in the Carbon/Et₄NBF₄/AN system in comparison to IL based electrolyte may be explained by the limited accessibility of pores in carbon materials. In case of Et₄NBF₄ electrolyte both ions are solvated by the acetonitrile molecule. It is worth noting that a comparison of the negative electrode in both electrolytes is not as significant as in case of the positive part. That suggests a greater influence of the solvation process of the tetrafluoroborate anion. The highest values of capacitances obtained for EMImBF₄ (underlined in Table 2) amount to 254–354 Fg⁻¹ for the AC295 carbon applied as the positive electrode. The highest values of capacitances for the negative electrode were recorded for carbon of 0.170 (163–197 Fg⁻¹). In contrast, capacitances obtained for EMImBF₄ as an electrolyte in carbon material-based EDLCs [23–25] fall within the range of 90–140 Fg⁻¹.

3.2. Asymmetric EDLC

Analysis of Figs. 2 and 4 as well as values in Table 2 show quite a different behaviour of the carbon material working as the negative or positive electrode. To improve the quality of the EDLC based on carbon materials tested, two carbons of the best characteristics were applied as positive and negative, respectively. The first step was to measure the performance of the EDLC based on AC290 carbon as the positive and AC170 as the negative electrode material. Obtained results facilitated the preparation of a mass balance of the carbon materials. Taking into account the differences in gravimetric capacitance of carbons AC290 and AC170, a 30% excess of the mass of the negative electrode was calculated. Results given in Table 2 show comparable specific capacitances of carbons tested, measured as separate electrodes. Figs. 5 and 6 present the results of the cyclic voltammetry measurement for both asymmetric electrochemical capacitors. Fig. 5A and B present capacities of

Table 2
Capacitances of carbon materials (Fg⁻¹) applied as electrodes in EDLC.

Electrolyte	Carbon materials	CV ^a (at 5 mV s ⁻¹)		EIS ^b (from 1 mHz)		Galvanostatic (0.2 Ag ⁻¹)		
		(-)	(+)	(-)	(+)	(-)	(+)	Cell
1M Et ₄ NBF ₄ in Acetonitrile	AC295	170	140	150	142	146	178	169
	AC170	162	147	154	156	157	189	184
	AC082	148	158	146	143	169	179	187
EMImBF ₄	AC295	181	261	132	354	179	254	210
	AC170	194	193	163	244	197	219	210
	AC082	160	224	153	190	194	249	220
	Asymmetric AC295(+) AC170(-)	177	227	167	191	184	236	211
	equal electrode mass							
	Asymmetric AC295(+) AC170(-)	164	217	167	190	172	253	212
	mass balanced							

^a Cyclic voltammetry.

^b Electrochemical impedance spectroscopy.

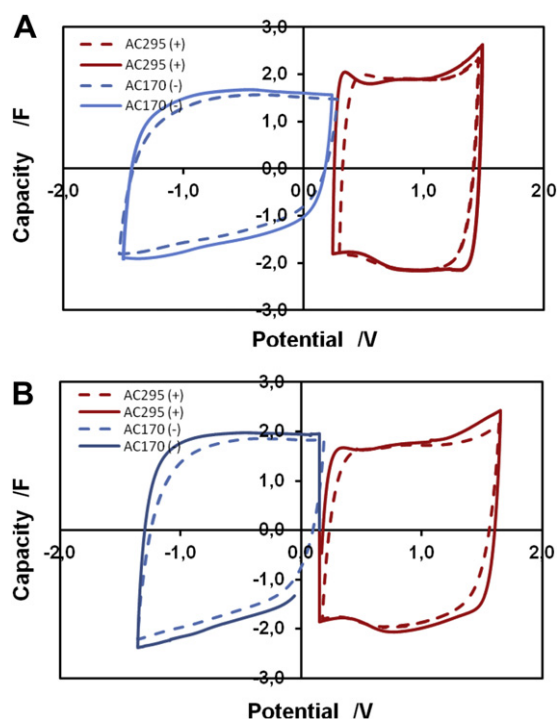


Fig. 5. Comparison of two asymmetric EDLCs with AC295(+) carbon as positive and AC170(–) as negative electrodes with equal masses (A) and with electrode mass balanced (B). EMImBF₄ as electrolyte. Cyclic voltammetry at 20 mV s^{–1} – dashed line and 10 mV s^{–1} – solid line.

electrodes provided by the 3-electrode cyclic voltammetry measurements for the asymmetric EDLC with the electrodes of equal mass and the mass balanced asymmetric EDLC (Fig. 5B) at a 10 mV s^{–1} scan rate (20 mV s^{–1} for the entire EDLC). An analysis of the figure shows a better matching of the working electrode characteristics in the case of the mass balanced EDLC. The effect of the increase in mass of the negative electrode results in an increased capacity of the EDLC devices. Fig. 6 shows cyclic voltammetry at a single sweep rate of 10 mV s^{–1} for both capacitors tested. In both EDLC cells the positive electrodes have identical masses of 10 mg.

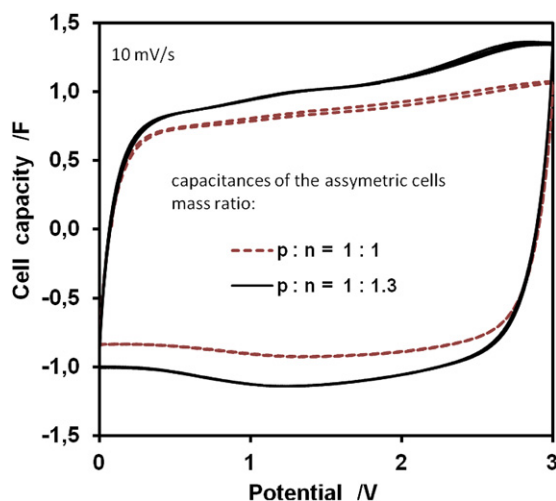


Fig. 6. Capacitances of asymmetric EDLC cells, with unbalanced (dashed line, carbon masses 9.0 ± 0.1 mg in each electrode) and balanced (solid line) masses of electrodes (positive 8.7 mg, negative 11.7 mg). EMImBF₄ as electrolyte.

Fig. 7 presents the frequency dependence on capacitance in both asymmetric capacitors. The different behaviour of the carbons selected as the positive and negative electrodes may be corrected by increasing the mass of the negative electrode, which results in better matching. Results of the galvanostatic cycles of the asymmetric EDLCs with and without the mass balance procedure carried out for over 2000 cycles shows a reduction of gravimetric capacitance at 75% of initial values and stabilisation after the first 1000 cycles.

3.3. Energy and power density

Energy and power density were determined using equations:

$$E = \frac{CV^2}{2m_c} \quad (1)$$

$$P = \frac{V^2}{4ESR \cdot m_c} \quad (2)$$

where V is the cell voltage applied, C is capacitance calculated from cyclic voltammetry at a 10 mV s^{–1} sweep rate of the full cell, ESR is equivalent series resistance taken from the impedance spectroscopy analysis, and m_{carb} is a sum of active masses of

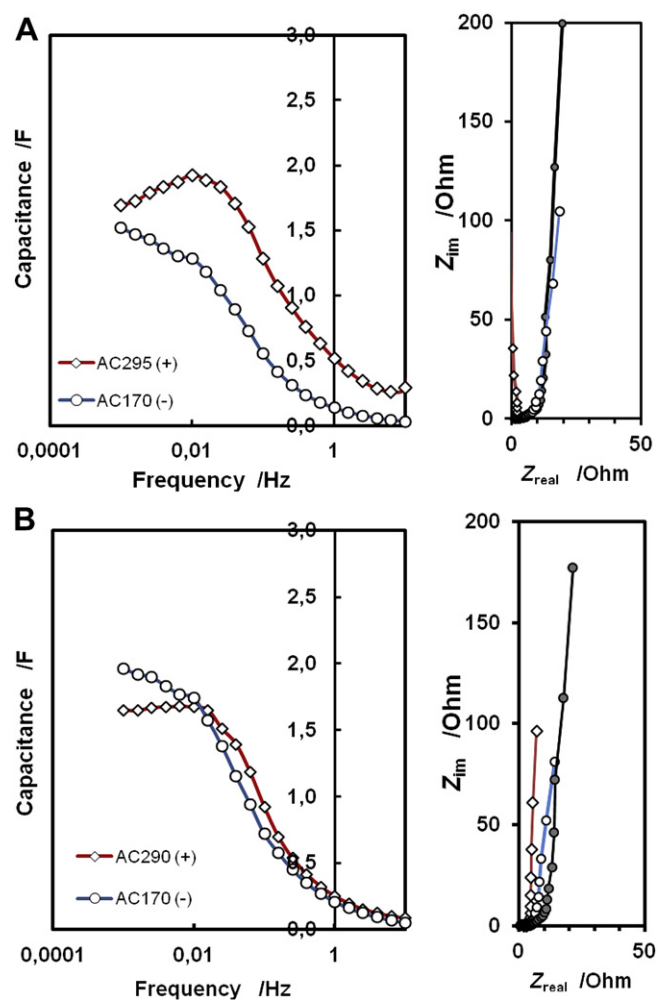


Fig. 7. Impedance analysis of the asymmetric EDLC cell with equal masses (9.0 ± 0.1 mg in each electrode) of both electrodes (A) and the asymmetric EDLC cell with mass balance (B) (positive 8.7 mg, negative 11.7 mg). EMImBF₄ as an electrolyte.

Table 3

Energy and power density of EDLC based on EMImBF₄ and different carbon materials.

Electrolyte	Carbon materials	Energy density [Wh kg ⁻¹]	Power density [kW kg ⁻¹]
EMImBF ₄	AC295	55.9	13.3
	AC170	57.3	25.6
	AC082	60.7	23.3
	Asymmetric AC295(+) AC170(-) equal electrode mass	64.2	27.8
	Asymmetric AC295(+) (8.7 mg) AC170(-) (11.7 mg) mass balanced	68.6	36.7

carbons of both electrodes. In all symmetric EDLCs masses of carbon materials were of ca. 9.0 mg, in case mass balanced asymmetric EDLCs active carbon contents of positive and negative electrodes were 8.7 mg and 11.7 mg, respectively. Table 3 presents results of calculations for appropriate parameters of the EDLC cell based on EMImBF₄ as an electrolyte. Inspection of Table 3 shows that optimisation of mass of the electrodes yields more efficient EDLCs.

4. Conclusions

1. A coconut-based carbon material of different pore distribution V_{mic}/V_{mez} rates was tested as positive and negative electrodes in EDLCs with EMImBF₄ as an electrolyte. The results show an extremely different behaviour of carbons with gravimetric capacitances of 150–350 Fg⁻¹.
2. Higher values of capacitances were observed for the capacitors based on EMImBF₄ rather than on the Et₄NBF₄/acetonitrile electrolyte.
3. Asymmetric EDLC capacitors produced from different carbons and the optimisation of electrode mass ratio were applied to improve electrochemical characteristics of the EDLC tested.
4. Optimisation of the EDLC results in an improvement of energy and power density of the EDLCs amounting to ca. 68 Wh kg⁻¹ and 36 kW kg⁻¹, respectively.

Acknowledgements

This work was supported by the Ministry of Science and Higher Education of Poland (Project no. N N507 284036).

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